ELSEVIER

Journal of Magnetism and Magnetic Materials 184 (1998) 62–66

journal of magnetism and magnetic materials

Magnetocaloric effect in the vicinity of magnetic phase transition

A.M. Tishin*

Department of Physics, M.V. Lomonosov Moscow State University, 119899 Moscow, Russian Federation

Received 22 October 1997; received in revised form 17 November 1997

Abstract

The paper discusses the adiabatic magnetization processes (magnetocaloric effect) in the region of magnetic phase transitions, based on known data about magnetic phase diagrams and the magnetocaloric effect of the rare-earth metals Gd and Dy. A correlation between an arrangement of lines of the magnetic phase transitions on (H, T) diagrams and a corresponding value of magnetocaloric effect were assumed.

PACS: 75.30.S; 75.30.K

Keywords: Magnetocaloric effect; Magnetic phase transition; Rare earth

The heavy rare earths are metals with well-studied magnetic properties (see, for example, Refs. [1,2]). The magnetic phase diagrams of these magnets have been intensively studied by X-ray [3] and neutron [4] scattering, heat capacity measurements [5] and other techniques. A general view of the phase diagrams strongly depends on the experimental techniques used as well as on the method of determination of a point of the phase change from experimental curves. Most of the currently practiced setups give different values of the phase transition points for the same sample. The comparison of the different procedures of determining the position of the phase transition point of gadolinium has been made in the Ref. [6]. Their value of Curie temperature, T_C, calculated from inflection points of experimental magnetic susceptibility and heat capacity is in excellent agreement with those obtained from magnetocaloric effect (MCE) and Arrot plots [6].

Practically, for studying (H, T) magnetic phase diagrams of different magnets the experimentalists operate under either isothermal or adiabatic conditions. The isothermal conditions can be easily achieved at the static and/or quasi-static magnetic field measurements. For example, under very slowly increasing the field in a situation when a magnet has the possibility to remain at zero field temperature due to heat exchange with the surroundings.

* Tel.: +7 095 939 3883; fax: +7 095 939 3588; e-mail: t@mpt.msk.ru.

0304-8853/98/$19.00
PII S0304-8853(97)01113-X

At the same time, under adiabatic conditions, the temperature of a magnet could be changed due to the magnetocaloric effect. For experimental measurements this situation is often observed when the sample is located inside a vacuum insert and/or at pulse fields. Up to the present, the experimental circumstances for exact realization of the quasi-adiabatic conditions in non-vacuum inserts are unknown. In accordance with data of Ref. [7], the transition between isothermal and quasi-adiabatic conditions occurs in a range of the rate of field increase from 20 to 200 T/s (for situation when the sample is located in liquid nitrogen or helium). It is shown [8] that for the nitrogen gas surrounding, the field sweep rate of about 90 T/s clearly corresponds to the adiabatic condition.

Consider an (H, T) phase diagram of a magnet at atmospheric pressure. At isothermal conditions the concrete magnetic state on the (H, T) diagram is determined by the value of the zero field temperature and applied magnetic field. In the adiabatic cases, when the initial temperature for a magnetization process can change due to MCE, the visualization of the (H, T) coordinates also requires the MCE value. In case, if an initial magnetic phase of a sample in the adiabatic conditions is changed by applying a magnetic field (for example, from antiferromagnetic (AFM) to ferromagnetic (FM) phase) the situation becomes more complicated. Especially, if the magnet can cross a line of first-order phase transition and/or the rate of field increase is too large (for example, such as 65 MT/s like in Ref. [9]).

In this paper, an analysis of the nature of the adiabatic heating of Gd and Dy in the vicinity of phase transition regions is presented. The adiabatic phase transformations under applied field will be discussed.

It has been established [6] that a value of zero field Curie temperature of Gd is 294 K. At the same time, it is well known (see, for example, Refs. [2,6]), that as the field H increases, the curves of the temperature dependences of magnetization $I(T)$ in ferromagnets are shifted towards higher temperatures. This indicates that there is a corresponding shift of the transition point (which should be located in the vicinity of the point of the maximum of magnetization derivative over temperature $\mathrm{d}I(T)/\mathrm{d}T$. The same also could be indicated by the shift of heat capacity and MCE anomalies in the phase transition region towards the high-temperature region as the field increases. However, up to the present, the exact value of this shift for different magnets has not been studied. Authors of Ref. [6] have shown that in a single crystal of Gd, the point of transition increases almost linearly with magnetic field at a rate of about 6 K/T in the field range from 2 to 7.5 T. Based on the experimental results of Ref. [6] the schematic view of the magnetic phase diagram of Gd is presented in Fig. 1. A point T_1 on this diagram corresponds to the zero field temperature. Points T_2 and T_3 lie at a field equal to H, but located on different sides of the line of ferromagnetism–paramagnetism (PM) phase transition.

This consideration refers directly to MCE, since the measurement of the value of temperature change $\Delta T(H, T)$ practically occurs at a change of the magnetic field from zero to a finite value H. Consider the case when MCE measurements are carried out in the vicinity of Curie point, T_C, for example, in the point T_1 (see Fig. 1). We suppose that the temperature T_1 is close to T_C, but lies outside the critical region. As field increases two situations could arise. First, if the value of MCE equals $\Delta T(H, T_1) = T_2(H) - T_1(0)$ or less, then Gd saves the initial magnetic phase. Second, if

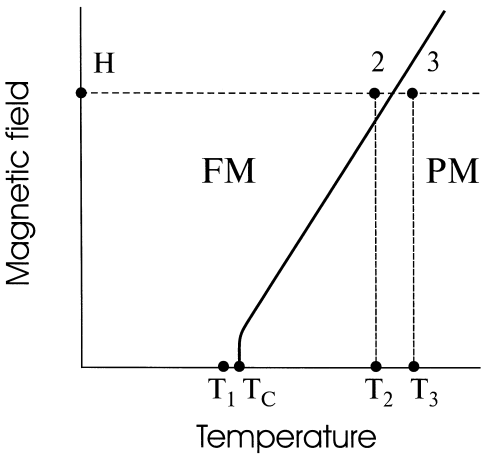

Fig. 1. Schematic view of the (H, T) magnetic phase diagram of Gd (based on the experimental data of Ref. [6]). Line of the magnetic phase transition is shown as a full line.

$\Delta T(H, T_1) = T_3(H) - T_1(0)$ or more, then the FM–PM phase transition could take place. The reason for this is that, in accordance with the experimental data of Ref. [6] the MCE in Gd near T_C point reaches about 19 K in the field 10 T.

Of course, it is obvious that in this simple case of FM–PM phase transition, the value of $\Delta T(H, T_1)$ should be less than or close to $T_2(H) - T_1(0)$, because Gd could not change FM structure to a PM as the field increased. An analysis of the experimental MCE data for Gd [6] supports this supposition. If temperature T_1 takes, for example, the value of 293 K (1 K below $T_C = 294$ K) then in accordance with the experimental data of Ref. [6] the value of $\Delta T(H, T_1) \approx 15.5$ K at a field of 7.5 T. The value of transition point at this field is located at about 339 K. Thus, the point T_2 ($H = 7.5$ T) lies about 30 K below the point of phase transition at 7.5 T. Even if in a large magnetic field the zero field Curie point transforms to a certain FM–PM transition region, then it is difficult to suppose that the T_C smearing is more than 30 K in a field 7.5 K.

The above consideration makes it possible to assume that first, the value of MCE in the vicinity of Curie point limited by the shift of Curie point at the field increases and second, under adiabatic conditions (without heat exchange with the surround) Gd cannot change the initial magnetic state. The rare-earth Gd is just one of the regular ferromagnets and, in our view point, the above conclusions should be also true for other ferromagnets. Thus, the extent of heating of a ferromagnet at adiabatic magnetizing process is determined by the behavior of the phase transition line.

The magnetic phase diagram of rare-earth Dy is much more complicated. For example, authors of Refs. [10,11] denote the line of the phase transition from FM to PM state, as a vertical stripe on the (H, T) diagram which starts from zero magnetic field and Néel temperature, $T_N \sim 180$ K. The other diagrams present this line as shifted to the region of low [5] or high [12] from a zero field transition point. Based on the experimental results of Refs. [5, 10–12] a scheme of the magnetic phase diagram of Dy in the temperature range from tricritical point $T_{TC} \approx 165$ K up to the paramagnetic phase $T > T_N$ is given in Fig. 2. The temperature region below T_{TC} will not be discussed here due to the fact

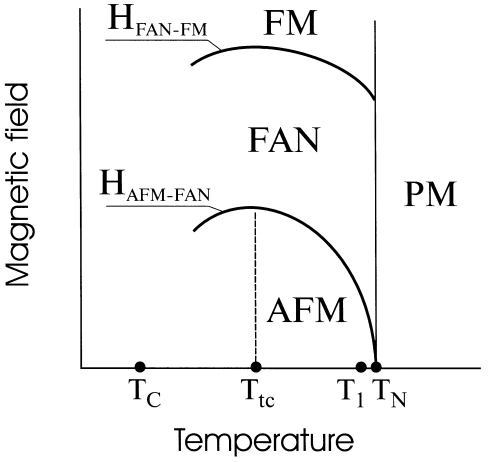

Fig. 2. Schematic view of the part of the (H, T) magnetic phase diagram of Dy (based on the experimental data of the Refs. [5,10–12]). Lines of the magnetic phase transitions are shown as full lines.

that the experimental data [5,10–12] present quite different views of the magnetic phase diagram in this temperature region. However, at zero field, it is certainly known that Dy has a helical antiferromagnetic structure from T_N down to $T_C \sim 90$ K [2,5].

Consider the adiabatic magnetization process at a temperature T_1 which is below, but like the case of Gd close to, T_N and when a value of applied magnetic field, H, at this point is less than that field of transition from AFM state to FAN phase, $H_{AFM–FAN}(T_1)$. Here FAN phase is an intermediate magnetic state which exists between AFM and FM phases. Although it is interesting for us to consider the temperature region when T_N–T_1 is of the order of 1–2 K, a detailed analysis of the situation is impossible, because the exact view of the (H, T) diagram at small fields in the vicinity of T_N is also unclear. However, it is known that the MCE values lie in the range ± 0.1–0.2 K up to the field ~ 1 T [13]. Thus, it seems unreal that Dy could change in this temperature and field region the initial magnetic phase due to MCE (for example, from AFM to FAN).

The second possible case is if the applied magnetic field, H, in the point T_1 is in the range from $H_{AFM–FAN}(T_1)$ to $H_{FAN–FM}(T_1)$, for example, $H = 1.5$ T (see Refs. [10,11]). At this field and

$T_1 = 177$ K, the MCE value is less than approximately 1 K [13]. Thus, the AFM structure of Dy could just be changed to FAN state. The following transition from FAN to PM (due to magnetocaloric heating of the sample at ~ 1 K) is practically impossible.

The consideration of the field region $H > H_{\mathrm{FAN-FM}}(T_1)$ leads us to the assumption that the line of the FM–PM phase transition should move to the right side if the MCE in these fields has a positive value. The shift of the line should be not less than the MCE value. For example, at temperature T_1, which is 1 K below T_N point, the MCE value approximately equals to 2 K at 2.5 T [13]. So, the FM–PM line should move to the right at least by ~ 1 K. The conclusion is in accordance with the diagram which is suggested in Ref. [12], and in contradiction with the data of Refs. [5,10,11]. Analysis shows that this shift should reach about 10 K or even more in the field of 6 T. However, it is necessary to note that the character of the behavior of the MCE in Dy used in Refs. [10,12] is unknown.

We could assume that in the vicinity of the zero field transition point, Gd and Dy could not change their FM and/or AFM phases to other magnetic states, due to MCE. This may be stated for ferromagnetic Gd based on the experimental results of Ref. [6] and, perhaps, should be valid more for Dy on the basis of new experimental measurements of the magnetic phase diagram and MCE on the same single crystalline sample.

In the case of Dy it is possible to assume that in the temperature range T_{TC}–T_N, the AFM state cannot be also modified by magnetocaloric heating to the FAN phase. The presumption is based on the known experimental fact that in the temperature range from T_N down to T_{TC}, the MCE has a close to zero or even negative value in the fields up to $H_{\mathrm{AFM-FAN}}$ [13]. So, in fields less than $H_{\mathrm{AFM-FAN}}$ the AFM state of Dy cannot be changed to the FAN or any other phase by MCE (AFM–FAN line moves to left side and any positive MCE in the fields close to $H_{\mathrm{AFM-FAN}}$ could 'help' the AFM state to intersect AFM–FAN line, see Fig. 2).

The character of the behavior of the MCE in a magnetic field, H, equal to the critical value, H_{cr}, could be explained in the framework of the thermodynamic relation for magnetic entropy, S_M, which can be easily obtained from Maxwell's formula [14]

$$(\mathrm{d}S_M/\mathrm{d}I)_T = -(\mathrm{d}H_{\mathrm{cr}}/\mathrm{d}T)_I,$$

where I is the magnetization. For the AFM–FAN phase transition in Dy the $\mathrm{d}I$ and $\mathrm{d}H_{\mathrm{cr}}/\mathrm{d}T$ have the positive and negative signs, respectively [11]. Thus, in an adiabatic process of the change of the lattice part of entropy, $\mathrm{d}S_L$, should have a negative sign ($\mathrm{d}S_L = -\mathrm{d}S_M$). This prediction is consistent with the experimental data of Ref. [11] about the MCE of Dy.

In conclusion, we have assumed that the FM and/or AFM phase states of a magnet cannot be changed in an adiabatic magnetizing process due to the non-zero MCE value, e.g. for additional shift of the initial temperature. The MCE cannot render any influence on the initial magnetic phase state, which at atmospheric pressure can be transformed just by applying the corresponding magnetic field $H \geqslant H_{\mathrm{cr}}$. On the other hand, it is known that in antiferro- and ferromagnets the high and low temperature region shifts of the AFM–FM and FM–PM phase transition lines occurs as the field increases (depending on the sign of the critical field value of phase transition derivative over temperature, $\mathrm{d}H_{\mathrm{cr}}(T)/\mathrm{d}T$). In our opinion, if the field is close to criticality, the sign of $\mathrm{d}H_{\mathrm{cr}}(T)/\mathrm{d}T$ determines the MCE value; a negative or close to zero MCE value in the AFM state and a positive one in the FM phase.

The results of this work are especially important for experimental studies of magnets with a large MCE value in the vicinity of a magnetic phase transition. It should be noted, however, that in the case of antiferromagnets these assumptions require in future careful experimental verifications.

Acknowledgements

The author thanks Prof. K.A. Gschneidner Jr. and Dr. V.K. Pecharsky for useful discussions.

References

[1] J. Jensen, A.R. Mackintosh, Rare Earth Magnetism, Structures and Excitations, Clarendon Press, Oxford, 1991.

[2] K.A. McEwen, in: K.A. Gschneidner Jr., L. Eyring (Eds.), Handbook on the Physics and Chemistry of Rare Earths, vol. 1, North-Holland, Amsterdam, 1991, p. 411.
[3] J. Bohr, D. Gibbs, D.E. Moncton, K.L. D'Amico, Physica A 140 (1986) 349.
[4] D.A. Tindal, M.O. Steinitz, T.M. Holden, J. Appl. Phys. 73 (1993) 6543.
[5] K.A. Gschneidner Jr., V.K. Pecharsky, 1997, private communication.
[6] S.Yu. Dan'kov, A.M. Tishin, V.K. Pecharsky, K.A. Gschneidner Jr., Phys. Rev. B 57 (1998) in print.
[7] R.Z. Levitin, V.V. Snegirev, A.V. Kopylov, A.S. Lagutin, A. Gerber, J. Magn. Magn. Mater. 170 (1997) 223.
[8] S.Yu. Dan'kov, A.M. Tishin, V.K. Pecharsky, K.A. Gschneidner Jr., Rev. Sci. Instr. 68 (1997) 2432.
[9] H. Nojiri, Y. Shimamoto, N. Miura, M. Hase, K. Uchinokura, H. Kojima, I. Tanaka, Y. Shibuya, Phys. Rev. B 52 (1995) 12749.
[10] R. Herz, H. Kronmüller, Phys. Stat. Sol. (a) 47 (1978) 451.
[11] S.A. Nikitin, A.M. Tishin, P.I. Leontiev, J. Magn. Magn. Mater. 92 (1991) 405.
[12] M.T. Alkhafaji, N. Ali, J. Alloys Compounds 250 (1997) 659.
[13] A.M. Tishin, PhD Thesis, M.V. Lomonosov Moscow State University, Moscow, 1988.
[14] M. Bailyn, A Survey of Thermodynamics, AIP Press, New York, 1994, Ch. 8.